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APPLICATION OF DYED SLAGS OF SILICOMANGANESE PRODUCTION TO MANUFACTURING OF GLASS-CERAMIC MATERIALS

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Time-temperature conditions for the periods of cooling and crystallization of flaming silicomanganese slag sare determined. It is shown that the results obtained can be applied to the production of glass-ceramic materials for construction purposes.

Development of the process technology of glass-ceramic production has revealed that the color of flaming slags varies (from lettuce- or dark-green to pale-blue) during cooling and crystallization periods and depends on the thermal history of the slag [1].

The color of silicomanganese (SM) slags as a function of the time-temperature conditions was studied on samples taken directly from the melt at different temperatures with subsequent hardening of the samples in air. The samples were taken from the slag ladle (0.6 m^3) using a 150 cm^3 sampler. The sample mass was 200 to 250 g. A "Promin'" pyrometer was used for slag temperature monitoring during sampling (see Table 1).

Cooled SM slags are conventionally divided into frozen (with different ratios of the crystalline and glassy phases) and vitreous or hardened slags. Crystallized slag variants (usually gray-green in color) are formed upon slow cooling of the flaming melt. The degree of their crystallization depends on the time-temperature conditions of cooling and can attain 90 – 96%.

Using data of chemical analysis we found that SM slags belong to the K_2O – MgO – CaO – FeO – MnO – Al_2O_3 – SiO_2 system. The slags usually contain sulfur mainly in a sulfide form (up to 1%) and two classical chromophores – iron and manganese oxides – in amounts of 0.3 – 0.6% and 14 – 16%, respectively. Iron and manganese oxides and sulfur compounds are typical glass dyes: the first two of ionic type and the latter of molecular type [2]. Fe(II) ions lend blue color, whereas Fe(III) ions make the slag yellow-green. The combined effect of Fe^{3+} and Fe^{2+} ions is a source of brown color under certain conditions. Iron sulfide lends the glass a brown or even black color. The color of glass-ceramic materials is manifested differently from glass because ion-chromophores enter the crystal lattice and the residual glassy phase as well. Crystallized slags (in fracture) are perceived as gray-green in color.

This color is rather stable since even upon 1-h heat treatment at 900°C it remains the same. This color is mainly attributed to the color of the minerals that form the crystal variant of the slag and their inability to transmit light due to the numerous boundaries between crystals, which are 10 – 1000 μm in size.

Data of petrographic studies reveal minerals of the pyroxene and plagioclase group, manganese sulfide, and residual glassy phase present in the crystallized slags. The glassy phase is almost colorless or light colored.

Thermal treatment of crystallized slag specimens revealed that the surface of the slag specimens gains a brownish color only at high temperatures (900 – 1200°C). Most probably this color can be attributed to a change in the valence of the Mn^{2+} ions to Mn^{3+}. Thermal treatment of the samples in bitstone of $NaNO_3$ at a temperature of 750 – 800°C leads to a stable green color of the surface, which makes it possible to consider this process as an analog of the process of production of manganese green [3].

Thus, crystallized slags exhibit a stable gray-green color both in the bulk and on the surface.

It is found that vitreous slags are formed upon rapid cooling of the flaming SM slag melt, e.g., upon pouring the melt on a metal substrate. This slag is almost free of crystalline constituents. Granulated slags obtained by pouring the flaming melt into water can also be classed with vitreous slags. Moreover, a vitreous slag can also be obtained upon remelting crystallized slag variants.

Unlike crystallized SM slags, which have a stable gray-green color, vitreous slags manifest a diversity of colors and are capable of changing colors.

TABLE 1

Sample	Sample color		Sampling temperature, °C
	reflected light	transmitted light	
1	Gray-green	–	1480
2	Lettuce	Pale orange	1420
3	Dark green	Colorless	1350

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The time-temperature conditions are the main factor determining the color of vitreous SM slags. Thus, the variety of colors observed for vitreous slags (when using a primary slag of silicomanganese production) is determined first and foremost by the cooling rate and initial temperature of the slag melt.

Experiments revealed that dark green and lettuce colors are most characteristic of vitreous slags. Dark green color will be formed if the melt temperature does not exceed 1100 – 1200°C.

Using petrographic data on the dark green modification of the vitreous slag we found that the slag (in addition to the glassy phase) contains manganese sulfide crystals (up to 5 – 10%) and filamentary crystals of the protostructure (no more than 10 – 15%).

Unlike the opacified lettuce modification, specimens of the dark green slag transmit light when the plate thickness is no more than 3 mm. These specimens are colorless in transmitted light. Transmission spectra of the dark green slag correlate with the light transmission curve that is characteristic of silicate glass dyed with Mn^{2+} ions (see Fig. 1).

The lettuce modification of the slag is formed at the moment of sharp (1 – 10 sec) cooling of the flaming melt from an initial temperature of no less than 1250 – 1300°C. Within the indicated temperature range, phase immiscibility occurs as a result of liquation. Here the melt viscosity can range within 5 – 20 Pa · sec, which promotes a rapid process of phase immiscibility. Proceeding from data of electron microscopy we found that segregation stratification results in formation of a system having two interpenetrating (bound) phases. Here slag specimens exhibit a lettuce color both on the surface and in the bulk.

Formation of microinhomogeneities of a liquation character in the slag melt is most probably attributable to diffusion processes. The different degrees of slag opacification observed upon slag cooling at different temperatures confirm this assumption. Thus, at a temperature of article formation of about 1100 – 1200°C liquation is not observed. Segregational stratification characterized by the numerous interfaces thus formed promotes intense scattering (opacification) of light flux, which is the origin of the opacity of the lettuce slag modification.

Thin (about 30 – 50 μm) slag plates transmit light, thus gaining a pale-orange color. Spectrophotometric studies revealed that the transmission curve has much in common with the dark green slag spectrum and differs only in the intensity of the maxima.

ESR spectra exhibit a pronounced *g*-factor, which equals two, thus confirming the bivalent state of Mn and Fe and their octahedral coordination.

As regards the crystalline phases the lettuce slag modification is virtually an amorphous glass. The only crystal phase constantly present in the samples of this slag modification contains individual α-MnS crystals as spherical inclusions and dendritic clusters (from 1 to 20 μm in size) having a rather high light refraction ($d = 2.60$ Å, $I = 10$; $d = 1.84$ Å, $I = 10$). The alabandine (α-MnS) content in the samples ranged within 5 – 10%. This crystal phase is probably formed at temperatures $T > 1500$°C, which substantially exceeds the article formation temperature (1300 – 1350°C).

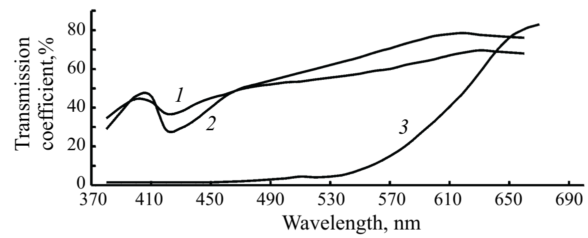

Fig. 1. Spectral characteristics of the SM slag: *1*) dark green slag, *2*) remelted slag, *3*) black glass.

The lack of features of large-scale crystallization and the complete amorphization of the melt indicate a rather high cooling rate of flaming SM slag. The combination of the green color of the MnS crystals and the light scattering due to liquation (the intensity of the liquation is attributable to a certain thermal inhomogeneity during formation of articles from the melt) lend a decorative effect of marbling.

The data on the dye behavior obtained for the dark green and lettuce slag modifications are almost identical.

Noticeable change in the slag color occurs starting with a temperature of 900°C: the surface gains a brown tone, and the green color in the bulk transforms to blue. On the fracture surface the specimen is matt and opaque, which indicates fine crystallization. At a temperature of 1100°C the surface becomes brownish black, which indicates oxidation of Mn^{2+} to Mn^{3+}. In the bulk the samples acquire an intense blue color.

The glassy (vitreous) variant of the SM slag can be obtained by remelting the crystallized slag. The remelted slag corresponds to a transparent amber-like glass. Spectral analysis showed that the slag stably holds its reduction potential and only after repeated remelting under oxidizing conditions does a saturated violet color (characteristic of Mn^{3+}; see Fig. 1) appear. This slag looks like black glass capable of near-infrared transmission only [4].

The dependences revealed can be used in developing structural glass-ceramic materials having rather high operational ability and decorative propeprties.

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